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(54) Title: CHEMICAL MECHANICAL POLISHING COMPOSITIONS AND METHODS RELATING THERETO

(57) Abstract: A polishing composition for removing metal by CMP comprises, a metal oxidizer, an oxide inhibitor, a complexing agent, and an engineered copolymer comprising, molecules of a first moiety having hydrophilic functional groups forming bonds with the metal, and molecules of a second moiety having hydrophobic functional groups that engage a polishing pad during CMP for the pad to remove the engineered copolymer from a surface of the metal, which enables removal of the metal by CMP while minimizing removal of the engineering copolymer from recessed circuit interconnects to minimize dishing.

CHEMICAL MECHANICAL POLISHING COMPOSITIONS AND METHODS RELATING THERETO

The invention relates to chemical mechanical polishing (CMP) of a semiconductor substrate. CMP refers to removal and planarization of thin films or layers on a semiconductor substrate, which form integrated circuits, multi-chip modules, capacitors and the like. The films or layers are classified according to three different materials: (i) a conductive metal layer; (ii) a barrier film or liner film between the conductive metal layer and an underlying dielectric layer; and (iii) an underlying dielectric layer having recessed metal lines that form metal circuit interconnects. During a CMP process, a polishing pad in combination with a fluid polishing composition removes a layer of metal, and polishes the semiconductor substrate with a smooth planar polished surface on which are manufactured successive layers. The successive layers themselves are polished by CMP.

The polishing composition comprises, a slurry having abrasive particles or a slurry, referred to as a reactive liquid, that comprises a substantially particle-free polishing composition. During CMP, the polishing pad undergoes motion relative to the semiconductor substrate, and applies friction to the substrate. The friction is combined with chemical reaction of the polishing composition with the surface of the substrate to remove material from the semiconductor substrate. Dishing refers to unwanted cavities that are caused by removal of metal from the circuit interconnects, during a CMP process. Erosion refers to excessive removal of dielectric material surrounding the circuit interconnects, during a CMP process.

US 6,117,775 discloses an inhibitor and a surfactant that suppress removal by etching and oxidation of circuit interconnects during CMP, while the inhibitor and surfactant adheres to a metal that is being removed by CMP. The inhibitor and surfactant are removed by friction applied by a polishing pad. The inhibitor comprises BTA, and the surfactant comprises, one of; polyacrylic acid, polyammoniumacrylate, polymethacrylic acid and polyammoniumacrylate.

The invention is directed to an engineered copolymer for suppressing dishing during CMP of a semiconductor substrate, wherein the engineered copolymer comprises, molecules of a first moiety having one or more hydrophilic functional groups forming bonds with the metal on the substrate surface, and molecules of a second moiety having

one or more hydrophobic functional groups that engage the polishing pad during CMP for the pad to remove the engineered copolymer from the surface of the metal being polished, which enables removal of the metal by CMP, while minimizing removal of the engineering copolymer from the recessed circuit interconnects to minimize dishing.

5 Embodiments of the invention will now be described by way of example with reference to the accompanying detailed description.

 The engineered copolymer is derived from one or more monomers forming molecules of a first moiety having one or more hydrophilic functional groups forming bonds with the metal on the substrate surface, and forming molecules of a second moiety
10 having one or more hydrophobic functional groups that engage the polishing pad during CMP for the pad to remove the engineered copolymer from the surface of the metal being polished, which enables removal of the metal by CMP, while minimizing removal of the engineering copolymer from the recessed circuit interconnects to minimize dishing. Hydrophilic functional groups are ionizable functional groups. Hydrophobic
15 functional groups are non-ionizable functional groups. The engineered copolymer enhances removal of metal from a substrate, while minimizing dishing of recessed metal circuit interconnects through controlled contact-mediated reactions with the substrate surface and the polishing pad surface.

 In an embodiment, the engineered copolymer is derived from one or more
20 monomers to provide hydrophilic functional groups that readily form strong bonds, e.g. coordinate covalent bonds, with the substrate surface during CMP. Further, the engineered copolymer is derived from one or more monomers to provide hydrophobic functional groups that provide structural rigidity to the copolymer molecules by van der Waals forces or other interactions. The rigidity of the engineered copolymer is adjusted
25 by varying the mole ratios of the monomers forming the functional groups. When two monomers are utilized to derive or synthesize the engineering copolymer, the mole ratio of each monomer can be varied from about 1:20 to about 20:1. When more than two monomers are used to generate the copolymer, the total of all mole ratios is 1. In an embodiment, wherein the engineered copolymer of the invention is derived from at least
30 two monomers, one monomer is polyethylenically unsaturated and serves as the extending agent or crosslinking agent in the copolymer.

According to an embodiment, the molecules of the first moiety comprises, hydrophilic functional groups of one or more of; carboxyl, hydroxyl, halogen, phosphonate, phosphate, sulfonate, sulfate, nitro and the like, to form bonds with the metal being removed by CMP.

5 According to an embodiment, at least one or more engineered copolymers are present up to about 1% by weight in a reactive liquid. The reactive liquid is a particle-free polishing composition that comprises, (i) up to about 15% by weight of an oxidizing agent; (ii) up to about 2% by weight of a corrosion inhibitor; and (iii) up to about 3% by weight of a complexing agent forming complex metal ions in the reactive liquid. Further,
10 the reactive liquid comprises, a pH under about 5.0, alternatively, a pH in a range of about 2.8 to about 4.2, and alternatively, a pH in a range of about 2.8 to about 3.8.

According to another embodiment, at least one or more engineered copolymers are present up to about 1% by weight in a polishing composition having abrasive particles. The composition comprises, (i) up to about 15% by weight of an oxidizing
15 agent; (ii) up to about 2% by weight of a corrosion inhibitor; (iii) up to about 3% by weight of a complexing agent, and (iv) up to about 3% by weight of abrasive particles. Further, the composition comprises, a pH under about 5.0, alternatively, a pH in a range of about 2.8 to about 4.2, and alternatively, a pH in a range of about 2.8 to about 3.8.

In an embodiment, the engineered copolymer is derived from a mixture of
20 monomers, for example, an acrylic acid monomer and methacrylic acid monomer, combined at a mole ratio in a range of about 1:20 to about 20:1, and alternatively in a range of about 1:1.

In another embodiment, the engineered copolymer is derived from a mixture of monomers, for example, a mixture of, two or more, ethylenically unsaturated monomers,
25 said mixture containing at least about 50% by weight of an unsaturated carboxylic acid monomer to form branched and/or unbranched copolymer molecules.

The unsaturated carboxylic acid monomer comprises, either an unsaturated monocarboxylic acid monomer or an unsaturated dicarboxylic acid monomer. An unsaturated monocarboxylic acid monomer refers to one of unsaturated carboxylic acid
30 monomers containing 3 to 6 carbon atoms per molecule with a single carboxylic acid group and water-soluble salts thereof. Suitable ethylenically unsaturated monocarboxylic acid monomers are, for example, acrylic acid, oligomeric acrylic acid,

methacrylic acid, crotonic acid, vinylacetic acid and derivatives thereof such as corresponding anhydrides, amides, esters and water-soluble salts thereof.

An unsaturated dicarboxylic acid monomer refers to one of unsaturated dicarboxylic acid monomers containing 4 to 8 carbon atoms per molecule, anhydrides of the cis-and trans- dicarboxylic acids, and water-soluble salts thereof. Suitable
5 unsaturated dicarboxylic acid monomers comprise, for example, maleic acid, fumaric acid, alpha-methylene glutaric acid, itaconic acid, citraconic acid, mesaconic acid, cyclohexenedicarboxylic acid, and derivatives such as corresponding anhydrides, amides, esters and water-soluble salts thereof.

10 In another embodiment, the engineered copolymer is derived from one or more of monoethylenically unsaturated monomers, such as, vinylaromatic monomers comprising, for example, styrene, α -methylstyrene, vinyltoluene, ortho-, meta- and para-methylstyrene, ethylvinylbenzene, vinylnaphthalene and vinylxylenes. The vinylaromatic monomer includes a corresponding substituted counterpart, for example, one of
15 halogenated derivatives, containing one or more halogen groups, such as fluorine, chlorine or bromine; and nitro, or, for example, derivatives of, cyano, alkoxy, haloalkyl, carbalkoxy, carboxy, amino and alkylamino.

In another embodiment, the engineered copolymer is derived from one or more of monoethylenically unsaturated monomers comprising, for example, nitrogen-containing
20 ring compounds, for example, vinylpyridine, 2-methyl-5-vinylpyridine, 2-ethyl-5-vinylpyridine, 3-methyl-5-vinylpyridine, 2,3-dimethyl-5-vinylpyridine, 2-methyl-3-ethyl-5-vinylpyridine, methyl-substituted quinolines and isoquinolines, 1-vinylimidazole, 2-methyl-1-vinylimidazole, N-vinylcaprolactam, N-vinylbutyrolactam and N-vinylpyrrolidone. Monoethylenically unsaturated monomers also comprise ethylene
25 and substituted ethylene monomers, for example: α -olefins such as propylene, isobutylene and long chain alkyl α -olefins (such as (C₁₀-C₂₀)alkyl α -olefins); vinyl alcohol esters such as vinyl acetate and vinyl stearate; vinyl halides such as vinyl chloride, vinyl fluoride, vinyl bromide, vinylidene chloride, vinylidene fluoride and vinylidene bromide; vinyl nitriles such as acrylonitrile and methacrylonitrile.

30 In another embodiment, the engineered copolymer is derived from the polymerization of one of acrylic monomers and one of alkyl methacrylate monomers. Examples of the alkyl methacrylate monomer wherein the alkyl group contains from 1 to

6 carbon atoms (also called the "low-cut" alkyl methacrylates), are methyl methacrylate (MMA), methyl and ethyl acrylate, propyl methacrylate, butyl methacrylate (BMA) and butyl acrylate (BA), isobutyl methacrylate (IBMA), hexyl and cyclohexyl methacrylate, cyclohexyl acrylate and combinations thereof. Examples of the alkyl methacrylate monomer wherein the alkyl group contains from 7 to 15 carbon atoms (also called the "mid-cut" alkyl methacrylates), are 2-ethylhexyl acrylate (EHA), 2-ethylhexyl methacrylate, octyl methacrylate, decyl methacrylate, isodecyl methacrylate (IDMA, based on branched (C₁₀)alkyl isomer mixture), undecyl methacrylate, dodecyl methacrylate (also known as lauryl methacrylate), tridecyl methacrylate, tetradecyl methacrylate (also known as myristyl methacrylate), pentadecyl methacrylate and combinations thereof. Also included in an embodiment are: dodecyl-pentadecyl methacrylate (DPMA), a mixture of linear and branched isomers of dodecyl, tridecyl, tetradecyl and pentadecyl methacrylates; and lauryl-myristyl methacrylate (LMA), a mixture of dodecyl and tetradecyl methacrylates. Examples of alkyl methacrylate monomers wherein the alkyl group contains from 16 to 24 carbon atoms (also called the "high-cut" alkyl methacrylates), are hexadecyl methacrylate (also known as cetyl methacrylate), heptadecyl methacrylate, octadecyl methacrylate (also known as stearyl methacrylate), nonadecyl methacrylate, eicosyl methacrylate, behenyl methacrylate and combinations thereof. Also useful are: cetyl-eicosyl methacrylate (CEMA), a mixture of hexadecyl, octadecyl, and eicosyl methacrylate; and cetyl-stearyl methacrylate (SMA), a mixture of hexadecyl and octadecyl methacrylate.

In another embodiment, the engineered copolymer is derived from one or more of, alkyl methacrylate monomers and acrylate monomers with a dialkylamino group in the alkyl radical, such as dimethylaminoethyl methacrylate, dimethylaminoethyl acrylate; dialkylaminoalkyl methacrylamide and acrylamide monomers, such as N,N-dimethylaminoethyl methacrylamide, N,N-dimethylaminopropyl methacrylamide, N,N-dimethylaminobutyl methacrylamide, N,N-diethylaminoethyl methacrylamide, N,N-diethylaminopropyl methacrylamide and N,N-diethylaminobutyl methacrylamide. Alkyl methacrylate and acrylate monomers with one or more hydroxyl groups in the alkyl radical, especially those wherein the hydroxyl group is found at the β -position (2-position) in the alkyl radical. Hydroxyalkyl methacrylate and acrylate monomers have a substituted alkyl group (C₂-C₆)alkyl, branched or unbranched Hydroxy-alkyl

methacrylate and acrylate monomers comprise, 2-hydroxyethyl methacrylate (HEMA), 2-hydroxyethyl acrylate, 2-hydroxypropyl methacrylate, 1-methyl-2-hydroxyethyl methacrylate, 2-hydroxypropyl acrylate, 1-methyl-2-hydroxyethyl acrylate, 2-hydroxybutyl methacrylate and 2-hydroxybutyl acrylate. A mixture of 1-methyl-2-hydroxyethyl methacrylate and 2-hydroxypropyl methacrylate, is known as "hydroxypropyl methacrylate" or HPMA.

In another embodiment, the engineered copolymer is derived from one or more of, amine-containing monomers comprising, for example, amide monomers, such as, dialkylaminoalkyl acrylamides or methacrylamides (for example, dimethylaminopropyl methacrylamide), N,N-*bis*-(dimethylaminoalkyl) acrylamides or methacrylamides, N- β -aminoethyl acrylamide or methacrylamide, N-(methylamino-ethyl)acrylamide or methacrylamide, aminoalkylpyrazine acrylamides or methacrylamides; acrylic ester monomers such as dialkylaminoalkyl acrylates or methacrylates (for example, dimethylaminoethyl acrylate or methacrylate), β -aminoethyl acrylate or methacrylate, N-(*n*-butyl)-4-aminobutyl acrylate or methacrylate, methacryloxyethoxyethylamine, and acryloxypropoxypropoxypropylamine; vinyl monomers such as vinyl pyridines; aminoalkyl vinyl ethers or sulfides such as β -aminoethyl vinyl ether, β -aminoethyl vinyl sulfide, N-methyl- β -aminoethyl vinyl ether or sulfide, N-ethyl- β -aminoethyl vinyl ether or sulfide, N-butyl- β -aminoethyl vinyl ether or sulfide, and N-methyl-3-aminopropyl vinyl ether or sulfide; N-acryloxyalkyloxazolidines and N-acryloxyalkyltetrahydro-1,3-oxazines such as oxazolidinylethyl methacrylate, oxazolidinylethyl acrylate, 3-(γ -methacryloxypropyl)tetrahydro-1,3-oxazine, 3-(β -methacryloxyethyl)-2,2-pentamethylene-oxazolidine, 3-(β -methacryloxyethyl)-2-methyl-2-propyl-oxazolidine, N-2-(2-acryloxyethoxy)ethyl-oxazolidine, N-2-(2-meth-acryloxyethoxy)-ethyl-5-methyl-oxazolidine, 3-[2-(2-methacryloxyethoxy)ethyl]-2,2-dimethyloxazolidine, N-2-(2-acryloxyethoxy)ethyl-5-methyl-oxazolidine, 3-[2-(meth-acryloxyethoxy)-ethyl]-2-phenyl-oxazolidine, N-2-(2-methacryloxyethoxy)ethyl-oxa-zolidine, and 3-[2-(2-methacryloxyethoxy)ethyl]-2,2-pentamethylene-oxazolidine.

In another embodiment, the engineered copolymer is derived from one or more of, monomers with an unsaturated sulfonic acid monomer selected from one or more of 2-acrylamido-2-methyl-1-propanesulfonic acid, 2-methacrylamido-2-methyl-1-propanesulfonic acid, 3-methacrylamido-2-hydroxy-1-propanesulfonic acid, allylsulfonic

acid, allyloxybenzenesulfonic acid, 2-hydroxy-3-(2-propenyloxy)propanesulfonic acid, 2-methyl-2-propene-1-sulfonic acid, styrene sulfonic acid, vinyl sulfonic acid, 3-sulfopropyl acrylate, 3-sulfopropyl methacrylate and water-soluble salts thereof.

According to an embodiment, an engineered copolymer is derived from acrylic acid
5 monomer and methacrylic acid monomer combined at a mole ratio in a range of about 1:20 to about 20:1, and alternatively, about 1:1 ($\pm 25\%$).

Accordingly, an engineered copolymer is derived from polymerization of one or more of, monomers selected from the aforementioned classes of monomers, including, random copolymers, branched copolymers, block copolymers and alternating
10 copolymers.

The engineered copolymer is used in a polishing composition for CMP together with a commercially available polishing pad, for example, a polishing pad described in US5,489,233 and US5,932,486 and US5,932,486.

Removal of material, e.g., copper, from a substrate surface during CMP utilizes a
15 polishing composition containing, a metal oxidizing agent, a corrosion inhibitor, e.g., benzotriazole, BTA, and molecules of an engineered copolymer derived from monomers having hydrophilic functional groups and hydrophobic functional groups. During CMP, the corrosion inhibitor molecules and the engineered copolymer molecules undergo redistribution and compete to form bonds with the metal surface on the substrate. The
20 metal surface comprises hydrated metal atoms and hydrated metal atom-corrosion inhibitor molecular complexes. For example, a surface of an exemplary copper layer on a substrate has hydrated copper atoms and hydrated copper atom-BTA complexes. The hydrophilic functional groups form strong bonds, e.g., coordinate covalent bonds. The hydrophobic functional groups form strong van der Waals bonds with known
25 nanoasperities on the polishing pad surface.

The engineered copolymer is added to conventional polishing compositions, in a manner now described. An oxidizing agent used in a polishing composition for CMP includes, but is not limited to, peroxides such as hydrogen peroxide, iodates such as potassium iodate, nitrates such as cesium nitrate, barium nitrate, ammonium nitrate,
30 and/or mixtures of ammonium nitrate and cesium nitrate, carbonates such as ammonium carbonate, and persulfates such as ammonium persulfate and/or sodium persulfate and perchlorates.

A complexing agent, disclosed by US5,391,258, includes a carboxylic acid containing two or more carboxylate groups with hydroxy groups. Further, a complexing agent includes, but is not limited to, straight chain mono- and dicarboxylic acids and their corresponding salts such as malic acid and malates; tartaric acid and tartarates; gluconic acid and gluconates; citric acid and citrates; malonic acid and malonates; formic acid and formates; lactic acid and lactates; phthalic acid and phthalates; and polyhydroxybenzoic acid and its salts. can also be used in the polishing composition.

Corrosion inhibitors used in polishing compositions for CMP include BTA (benzotriazole) and TTA (tolyltriazole) or mixtures thereof. Other inhibitors that are suitable for use include: 1-hydroxybenzotriazole, N-(1H-benzotriazole-1-ylmethyl)formamide; 3,5-dimethylpyrazole; indazole; 4-bromopyrazole; 3-amino-5-phenylpyrazole; 3-amino-4-pyrazolecarbonitrile; 1-methylimidazole; Indolin QTS and the like.

A polishing composition for CMP is substantially particle-free or, alternatively, contains abrasive particles of a material that includes, but is not limited to, alumina, silica, ceria, germania, diamond, silicon carbide, titania, zirconia and various mixtures thereof. In an embodiment, the polishing composition of the invention does not contain any abrasive particles. In another embodiment, the polishing composition contains low levels of abrasives in a range from about 0 to about 3%, with an average particle diameter less than 50 nm. In other embodiments, the weight % of abrasive can be up to about 50%.

Optionally, a polishing composition for CMP may contain pH buffers such as amines, and may contain surfactants, deflocculants, viscosity modifiers, wetting agents, cleaning agents and the like.

The following examples illustrate various aspects of the invention. All parts and percentages are on a weight basis (i.e., by weight of the polishing composition) and all molecular weights are determined by gel permeation chromatography (GPC) and are weight-average molecular weights unless otherwise indicated.

EXAMPLE 1

Engineered copolymers I and II were derived or synthesized as described below. All molecular weights were determined utilizing GPC analysis according to the

following procedure. Molecular weight Determination: Samples were dissolved in 0.02M sodium dihydrogen phosphate at pH 7 at a concentration of approximately 0.1% w/v and shaken for 10 minutes, followed by filtration through a 0.45 micron PTFE polytetrafluoroethylene membrane filter. The analysis was performed by injecting 100
5 microliters of this solution into a 2-column set consisting of a TosoHaas TSKgel GMPWx1 and a TosoHaas TSKgel G2500PWx1 and a TosoHaas TSKgel G2500 Wx1 30 cm x 8 mm column, held at 40 C. The mobile phase used was this solution at a flow rate of 1 ml/min. Detection was via a differential refractive index measurement. The system was calibrated with narrow poly(acrylic) acid standards.

10 **Engineered Copolymer I :** To a 1 liter, 4-neck flask equipped with a mechanical stirrer, a reflux condenser, a thermocouple, and septum inlets was added 575.00 g (grams) deionized (D.I.) water and 5.00 g of 0.15 weight % $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. To this stirred solution at 60°C, 20.00 g of a monomer mixture containing 109.00 g of glacial methacrylic acid and 91.00 g of glacial acrylic acid was added. At 65°C, 0.50
15 g of sodium persulfate in 10.00 g D.I. water and 4.00 g sodium metabisulfite in 30.00 g D.I. water were added linearly and separately over 130 min. Ten minutes later, the remaining monomer mixture was added linearly over 120 min., at 72°C. After addition, the solution was held at temperature for 10 min., then cooled to 62°C. Next, 0.12 g of sodium persulfate in 5.00 g D.I. water was added. The solution was held for 10 min. and
20 the procedure repeated. The stirred solution was adjusted with 20.20 g of 50% sodium hydroxide and 2.70 g of 30% hydrogen peroxide. Next, 0.25 g of isoascorbic acid in 5.00 g D.I. water was added. The solution was held for 5 min. and the procedure repeated. The aqueous copolymer solution at pH 3.8 had a solids content of 24.3%, 548 ppm, parts per million, of acrylic acid, no detectable methacrylic acid and a molecular
25 weight (MW) of 178,700 with a corresponding mole ratio.

Engineered Copolymer II: To a 1 liter, 4-neck flask equipped with a mechanical stirrer, reflux condenser, thermocouple, and septum inlets, was added, 575.00 g of D.I. water and 5.00 g of 0.15 weight % $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. To this stirred solution at 72°C, 1.00 g of sodium persulfate in 10.00 g D.I. water, 12.00 g sodium
30 metabisulfite in 60.00 g D.I. water and a mixture containing 109.00 g of glacial methacrylic acid and 91.00 g of glacial acrylic acid were added linearly and separately

over 120 min. After addition, the solution was held at temperature for 10 min., cooled to 62°C and followed by the addition of 0.12 g sodium persulfate in 5.00 g D.I. water. The solution was held at temperature for 10 min. and another 0.12 g of sodium persulfate in 5.00 g D.I. water was added. The stirred solution was adjusted with 20.20 g of 50% sodium hydroxide and 6.00 g of 30 % hydrogen peroxide. Next, 0.25 g of isoascorbic acid in 5.00 g D.I. water was added. The solution was held for 5 min. and the procedure repeated. The aqueous copolymer solution at pH 3.6 had a solids content of 24.3%, 426 ppm of acrylic acid, no detectable methacrylic acid and a MW of 28,800 with a corresponding mole ratio.

10 **Engineered Copolymer IIA.** To a 1 liter, 4-neck flask equipped with a mechanical stirrer, reflux condenser, thermocouple, and septum inlets was added 500.00 grams (g.) deionized (DI) water and 5.00 g. of 0.15 weight % $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. To this stirred solution at 90°C, 0.80 g. of sodium persulfate in 10.00 g. of DI water was added. After holding five minutes at 90°C, 12.00 g. of a monomer mixture containing 67.70 g. of glacial methacrylic acid and 132.30 g. of glacial acrylic acid was added. Five minutes later, at 92°C, 7.20 g. of sodium persulfate in 40.00 g. DI water, 2.00 g. sodium hypophosphite in 20.00 g. DI water and the remaining monomer mixture were added separately and linearly over 120 min. After addition, the solution was held at temperature for 30 min., then cooled to 70°C. Next, 20.20 g. of 50 % sodium hydroxide was added, dropwise. The aqueous copolymer solution at pH 3.6 had a solids content of 26.8%, no detectable methacrylic acid or acrylic acid and a molecular weight (Mw) of 29,600 with a corresponding mole ratio.

25 **Engineered Copolymer IIB.** To a 1 liter, 4-neck flask equipped with a mechanical stirrer, reflux condenser, thermocouple, and septum inlets was added 410.00 grams (g.) deionized (DI) water and 5.00 g. of 0.15 weight % $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. To this stirred solution at 92°C, 10.00 g. sodium persulfate in 60.00 g. DI water was added linearly over 122 minutes. Two minutes later, at 92°C, 1.50 g. sodium hypophosphite in 20.00 g. DI water and a monomer mixture containing 147.20 g. glacial methacrylic acid and 52.80 g. glacial acrylic acid were added separately and linearly over 120 min. After addition, the solution was held at temperature for 30 min., and then cooled to 70°C. Next, 20.20 g. of 50 % sodium hydroxide was added, dropwise. The aqueous copolymer

solution at pH 3.8 had a solids content of 29.8%, no detectable methacrylic acid or acrylic acid and a molecular weight (Mw) of 19,500 with a corresponding mole ratio.

Each of the engineered copolymers I, II, IIA and IIB was combined with a polishing composition, which was used in CMP to polish respective copper patterned wafers on an AMAT Mirra polishing machine. Polishing by CMP was performed under the following conditions: First step at 5 psi down force, 93 rpm platen speed and 87 rpm carrier speed for 60 seconds; Second step at 3 psi down force, 93 rpm platen speed, 87 rpm carrier speed for 60 seconds. The first step of polishing was performed until endpoint was achieved on the AMAT Mirra as determined by the Mirra endpoint detection system. The second polishing step was terminated when the endpoint curve slope was zero. An IC1000 (X-Y grooved) polishing pad available from Rodel, Inc., Newark, Delaware was used for each polishing test. The slurry flow rate was held constant at 250 ml/min during each polishing test. A Tencor P1 profilometer was used to measure dishing of 100 μ m lines in the center, middle and edge of each test wafer. The data obtained during the various polishing tests are summarized in Table 1 below.

TABLE 1

| Sample | pH | Removal Rate (Angstroms/min) | Average Dishing (Angstroms) | Residuals |
|---------|-----|---------------------------------|-----------------------------------|--------------------------|
| Control | 3.1 | 3,435 | 1,300 | Significant residuals |
| A1 | 3.0 | 5,394 | 1,920 | Clear/no residuals |
| A2 | 3.5 | 3,285 | 1,580 | Clear/no residuals |
| B1 | 3.0 | 4,611 | 1,350 | Clear/no residuals |
| B2 | 3.5 | 3,200 | 990 | Clear/no residuals |
| C1 | 3.0 | | 2014 | Clear/no residuals |
| D1 | 3.0 | | 831 | Significant residuals |

All polishing compositions contained 9% hydrogen peroxide, 0.3% BTA and 0.22% malic acid.

The Control contained 0.18% of a 1:1 mixture of polyacrylic acids with number average molecular weights of 250,000 and 30,000, respectively.

Polishing compositions A1 and A2 contained 0.36% of active engineered copolymer I.

5 Polishing compositions B1 and B2 contained 0.36% of active engineered copolymer II.

Polishing composition C1 contained 0.18% of active engineered copolymer IIB and Polishing composition D1 contained 0.18% of active engineered copolymer IIA.

10 The remaining weight percentage of each polishing composition comprised water.

The data in Table I indicates that a copolymer containing a 7:3 molar composition of polymethacrylic acid to polyacrylic acid clears the wafer of all copper residue whereas a copolymer containing a 3:7 molar composition of polymethacrylic acid to polyacrylic acid does not clear all the copper residue. Accordingly, clearing of copper residuals requires at least an equimolar ratio 1:1 or greater ratio, of the polymethylacrylic acid in the copolymer.

EXAMPLE 2

20 Engineered copolymers III, IV and V were synthesized as described below.

Engineered Copolymer III: To a 2 liter, 4-neck round bottom flask equipped with a mechanical stirrer, reflux condenser, thermocouple, and septum inlets was added 700.00 g (grams) of D.I. water and 6.00 g of 0.15 weight % $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. To this stirred solution at 80°C, 13.50 g of sodium persulfate in 100.00 g D.I. water; 75.00 g of 25 50% sodium hydroxide and a mixture containing 106.00 g of glacial methacrylic acid and 160.00 g hydroxyethyl methacrylate were added linearly and separately over 125 min. as the kettle temperature was allowed to rise to 92°C. After addition, the solution was held for 30 min. and 0.20 g sodium persulfate in 1.00 g D.I. water was then added. The solution was held at temperature for 10 min. and the procedure repeated with 0.50 g 30 sodium persulfate in 4.00 g D.I. water. The aqueous copolymer solution at pH 6.2 had a solids content of 25.9%, 1450 ppm methacrylic acid and a MW of 20,100 with a corresponding mole ratio.

Engineered Copolymer IV: To a 2 liter, 4-neck round bottom flask equipped with a mechanical stirrer, reflux condenser, thermocouple, and septum inlets was added 577.00 g of D.I. water and 3.00 g of 0.15 weight % $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. To this stirred solution at 88°C, 10.20 g of sodium persulfate in 50.00 g D.I. water, 99.00 g of 50% sodium hydroxide and a mixture containing 206.50 g of glacial methacrylic acid and 132.60 g hydroxyethyl methacrylate were added linearly and separately over 125 min. After addition, the solution was held at 88 to 90°C for 55 min. and 1.10 g sodium persulfate in 7.20 g D.I. water was then added and the solution held at temperature for 60 min., cooled to 65°C and diluted with 40.00 g D.I. water. The aqueous copolymer solution at pH 5.9 had a solids content of 34.0 %, 397 ppm methacrylic acid and a MW of 14,100 with a corresponding mole ratio.

Engineered Copolymer V: To a 2 liter, 4-neck round bottom flask equipped with a mechanical stirrer, reflux condenser, thermocouple, septum inlets and containing 800.00 g D.I. water at 86°C was added; 0.25 g of inhibitor, 70.80 g of a 1.75 wt % surfactant solution, 68.30 g of a monomer emulsion, containing 300.00 g D.I. water, 2.20 g of a 30% surfactant solution, 325.00 g of methyl methacrylate, and 4.20 g of glacial methacrylic acid followed by 2.30 g of sodium persulfate in 16.7 g D.I. water. After addition, the kettle material was held at 86°C for 15 minutes. To the remaining monomer emulsion 23.00 g of a 30% surfactant solution, 248.50 g of glacial methacrylic acid, and 5.70 g of n-dodecyl mercaptan was added followed by 30.00 g of rinse water. This monomer emulsion was added linearly over 120 min. to the kettle at 85°C. After addition, the reaction was held at temperature for 15 min., cooled, then filtered through 100/325 mesh screens. The emulsion polymer at pH 2.8 had a solids content of 31.4%, 331 ppm of methacrylic acid, 171 ppm of methyl methacrylate, a MW of 56,400 with a corresponding mole ratio, and a particle size of 105 nm.

Table 2 summarizes removal rate data obtained, according to the method of the invention, utilizing polishing compositions containing engineered copolymers III, IV and V. All polishing compositions contained 0.36% of the respective engineered copolymer, 9% hydrogen peroxide, 0.3% BTA, and 0.22% malic acid. The remaining weight percentage of each polishing composition comprised water.

Table 2

| Engineered Copolymer | Molecular Weight (MW) | Removal Rate (Angstroms/minute) |
|-----------------------------|------------------------------|--|
| III | 20,100 | 1,500 |
| IV | 14,100 | 3,000 |
| V | 56,400 | <1,000 |

The data in Table 2 illustrate that removal rates in excess of 1,000 Angstroms per minute are obtained utilizing the invention. The exemplified polishing compositions respectively comprised engineered copolymers made from a mixture of monomers, wherein the mixture has greater than 50 mole% of acid-containing monomers.

A polishing composition for CMP is provided with an engineered copolymer comprising, molecules of a first moiety having one or more hydrophilic functional groups forming bonds with the metal on the substrate surface, and further comprising, molecules of a second moiety having one or more hydrophobic functional groups that engage the polishing pad during CMP for the pad to remove the engineered copolymer from the surface of the metal being polished, which enables removal of the metal by CMP, while minimizing removal of the engineering copolymer from the recessed circuit interconnects to minimize dishing.

CLAIMS:

1. A polishing composition for removing metal by CMP comprises, a metal oxidizer, an oxide inhibitor and a complexing agent, further characterised by;
an engineered copolymer comprising, molecules of a first moiety having
5 hydrophilic functional groups forming bonds with the metal, and further comprising, molecules of a second moiety having hydrophobic functional groups that engage a polishing pad during CMP for the pad to remove the engineered copolymer from a surface of the metal, which enables removal of the metal by CMP, while minimizing removal of the engineering copolymer from recessed circuit interconnects to minimize
10 dishing.
2. The polishing composition as in Claim 1, wherein said engineered copolymer is selected from a group consisting of; random copolymers, block copolymers, branched copolymers and alternating copolymers.
3. The polishing composition as in Claim 1 wherein the engineered copolymer is
15 present at a concentration up to about 1% by weight.
4. The polishing composition as in Claim 1, further characterised by; abrasive particles up to about 3% by weight.
5. A polishing composition as in Claim 1 wherein the engineered copolymer is derived from an acrylic acid monomer and a methacrylic acid monomer at a mole ratio of
20 acrylic acid monomer to methacrylic acid monomer in a range of, about 1:20 to about 20:1.
6. A polishing composition as in Claim 1 wherein the engineered copolymer is derived from a mixture of ethylenically unsaturated monomers.
7. A polishing composition as in Claim 7 wherein the engineered copolymer has
25 a concentration up to about 1% by weight, the oxidizing agent has a concentration up to about 15% by weight, the complexing agent has a concentration up to about 3% by weight, and the inhibitor has a concentration up to about 2% by weight.
8. A method for removing metal by CMP, comprising: polishing the metal with a polishing pad and a polishing composition, the polishing composition having, a metal
30 oxidizer, an oxide inhibitor, a complexing agent, and an engineered copolymer comprising, molecules of a first moiety having hydrophilic functional groups forming bonds with the metal, and further comprising, molecules of a second moiety having

hydrophobic functional groups that engage the polishing pad during CMP for the pad to remove the engineered copolymer from a surface of the metal, which enables removal of the metal by CMP while minimizing removal of the engineering copolymer from recessed circuit interconnects to minimize dishing.

- 5 9. The method as in Claim 8 wherein the polishing composition further comprises abrasive particles of a concentration up to about 3% by weight.

